Compounds with Gold-Antimony Bonds

THEIR POTENTIAL ACTIVITY IN HOMOGENEOUS CATALYSIS

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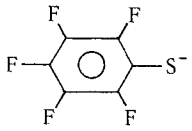
A new field of interest in the chemistry of gold has been opened up by the preparation and characterisation of complexes containing gold-to-antimony metal-metal bonds. These exhibit catalytic properties similar to those of the well known platinum-tin complexes, and may also have potential value in the homogeneous hydrogenation of olefins.

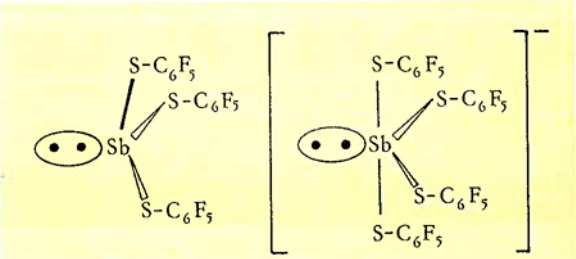
In the last ten years numerous papers and communications have been published concerning the characterisation and catalytic properties of compounds containing transition metal-tin bonds (1). In particular the platinum(II) complexes of the $SnCl_3^-$ ligand, e.g. $(Ph_3P)_2Pt(Cl)SnCl_3$ and $PtCl_2(SnCl_3)_2^{2-}$, have received considerable attention because of their catalytic activity in the homogeneous hydrogenation of olefins (2). This activity is associated with the π-accepting properties of the $SnCl_3^-$ ligand (3) which help the platinum(II) to form a sufficiently labile pentacoordinated complex containing both a hydrogen atom and the olefin coordinated to the metal (4), thus allowing the reaction between the two to take place at the platinum via an alkyl intermediate (5).

Although gold(III) has the same valence electronic configuration as platinum(II), $5d^8$, the formation of equivalent Au(III)-$SnCl_3$ derivatives is not possible because gold(III) is reduced by the stannous chloride. Thus the only known gold-tin complexes are of the type $(Ph_3P)_nAu\text{-}SnCl_3$ (where n=1,2,3) (6) or polynuclear species such as $Au_5(PPh_3)_4.SnCl_3$ (7). Since the $SnCl_3^-$ ligand is too strong a reducing agent it was of interest to use in its place the isoelectronic and isostructural trichloroantimony, $SbCl_3$ being a less effective reducing agent than $SnCl_3^-$. But none of the expected gold(III)-to-antimony bonded complexes could be isolated from $SbCl_3$ and $AuCl_4^-$ or $AuBr_4^-$ mixtures in ethanol, acetone or tetrahydrofuran. In this respect it should be pointed out that only a few chloroantimony-transition metal complexes are known (8), probably because of the relative inertness of the electronic lone pair of Sb(III).

Taking into account that the replacement of the chlorides around Sb(III) by a ligand having stronger π-electron withdrawing properties should strengthen the gold-antimony bond by way of π-back bonding, we have prepared and characterised (9) the species SbX_3 (pyramidal), SbX_4^-, SbX_3Cl^- and $SbX_2Cl_2^-$ (pseudo-trigonal bipyramidal) where $X^- = C_6F_5S^-$, the pentafluorothiophenoxide ion



which is indeed well known for its pseudo-halide behaviour and its strong-electron withdrawing properties (9, 10).

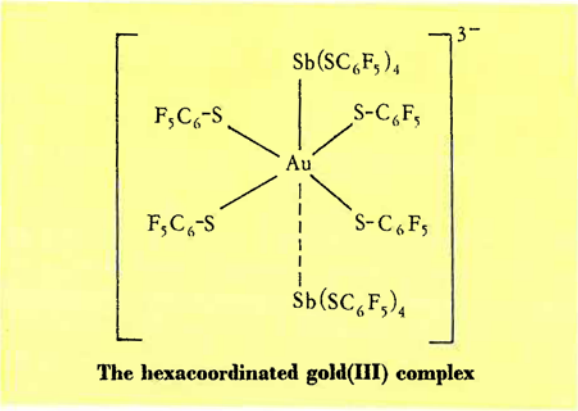


Stereochemistry of the SbX_3 and SbX_4^- species

Then we have studied various reactions of SbX_3, SbX_4^-, SbX_3Cl^- or $SbX_2Cl_2^-$ with the square planar complexes $AuCl_4^-$ or AuX_4^-, mostly in ethanol under nitrogen. The three following tetraphenylarsonium salts have been obtained and isolated:

(a)	$[Ph_4As]_3[AuX_4(SbX_4)_2]$	very deep red
(b)	$[Ph_4As]_3[AuX_4(SbX_3Cl)_2]$	deep red
(c)	$[Ph_4As]_3[AuX_4(SbX_2Cl_2)_2]$	orange red

These are quite stable when kept dry under nitrogen, but they decompose slowly in solution at room temperature. Their characterisation by elemental analysis, X-ray powder photographs, conductance measurements, infra-red and Raman spectroscopy and ^{19}F n.m.r. shows that the complex anions in these salts are hexacoordinated gold(III) species in the solid state with two Au-Sb bonds (one strong and one weak):



The hexacoordinated gold(III) complex

In view of the physical data obtained on these compounds it is not possible to assign them a more detailed structure. In solution, there occurs the complete dissociation:

$$[AuX_4(SbX_4)_2]^{3-} \rightarrow [AuX_4(SbX_4)]^{2-} + SbX_4^-$$

so that the complex anion is now a five-coordinated gold(III) species containing only one Au-Sb bond.

The Au-Sb bonds in compounds (a), (b) and (c) are essentially characterised by their infra-red and Raman stretching frequencies:

ν(Au-Sb) = 181 cm^{-1} in (a), 187 cm^{-1} in (b) and 191 cm^{-1} in (c)

The gold-antimony systems seem to be potential homogeneous catalysts for the hydrogenation of olefins. Indeed, ethylene is hydrogenated to ethane by a deep red ethanolic solution of $HAuCl_4$ or $HAuX_4$ ($\sim 10^{-3}$M) and SbX_3 taken in large excess ($\sim 10^{-2}$M) at 0°C and 1 atmosphere total hydrogen pressure. It is necessary to operate with rigorously deoxygenated ethanol and at low temperature, otherwise precipitates are formed and gold metal tends to deposit. A more detailed study of these catalytic properties is under progress.

Thus by using the strong π-electron withdrawing ligand $X^- = C_6F_5S^-$ in place of the chloride ion it is possible to obtain gold(III)-to-antimony bonded complexes which are the only known antimony analogues of the chlorotin-platinum(II) derivatives and which seem to exhibit the same catalytic properties in the homogeneous hydrogenation of olefins.

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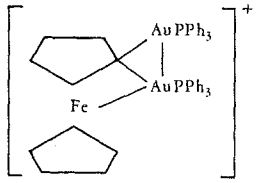
New Organometallic Compounds with a Gold-Gold Bond

A new series of organogold compounds has been synthesised in which there are two gold atoms per molecule bonded with one another directly. These have the general formula $[R(AuPPh_3)_2]^+[BF_4]^-$, where $R = C_6H_5$, p-$CH_3C_6H_4$, $C_5H_5FeC_5H_4$, and derivatives such as $C_5H_5FeC_5H_3OCH_3$.

These complexes, reported by A. N. Nesmeyanov, E. G. Perebalova, K. I. Grandberg, D. A. Lemenovskii, T. V. Baukova and O. B. Afanasova of the Moscow University Department of Organic Chemistry (*Vest. Moskov. Univ., Ser. II, Khim.*, 1973, **14**, (4), 387–399), are obtained when $^+AuPPh_3$ is generated in the presence of $RAuPPh_3$. An example is the reaction of HBF_4 with ferrocenyltriphenylphosphinegold $C_5H_5FeC_5H_4AuPPh_3$, which gives $[C_5H_5FeC_5H_4(AuPPh_3)_2]^+[BF_4]^-$.

The structure of these complexes has been investigated by nuclear magnetic resonance, infra-red and ultra-violet spectroscopy, and in the case of the ferrocenyl complex by X-ray crystallography (V. G. Andrianov, Yu. T. Struchkov and E. R. Rosinskaya, *J. Chem. Soc., Chem. Commun.*, 1973, 338). This is the first X-ray study on a ferrocene derivative with a direct iron-to-metal bond and the structure is as shown here. It is also the first known example of a cyclopentadienyl ring bridging (*exclusively* through one of its carbon atoms) *two* metal (Au) atoms.



These compounds undergo two main types of reaction involving either one or both of the $AuPPh_3$ groups.

An example of the first type is the reaction of PPh_3 with the p-tolyl complex (i.e. $R = p$-$CH_3C_6H_4$), which gives $[Ph_3PAuPPh_3]^+$ and $CH_3C_6H_4AuPPh_3$. The relative stabilities of ions of the general formula $[LAuPPh_3]^+$ is discussed for a number of ligands L. The second type involves reaction with other organometallic complexes and results in the interchange of organic radicals.

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